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REPORT

CD NO.

COUNTRY	USSR	DATE OF INFORMATION	1950
SUBJECT	Scientific - Physics, polarography	DATE DIST.	29 Aug 1950
HOW PUBLISHED	Bimonthly periodical		
WHERE PUBLISHED	Moscow	NO. OF PAGES	4
DATE PUBLISHED	May/Jun 1950	SUPPLEMENT TO REPORT NO.	
LANGUAGE	Russian		

THIS IS UNEVALUATED INFORMATION

SOURCE Zhurnal Analiticheskoy Khimii (Journal of Analytical Chemistry), Vol V, No 3, 1950.

REVIEW OF SOVIET PROGRESS IN THE POLAROGRAPHY OF ORGANIC COMPOUNDS

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This is a digest of review of recent Soviet improvements in polarographic technique and polarographic appliances. These improvements are largely based on research done in the USSR and reflect a demand for efficient analytical and automatic plant control appliances, particularly in branches of chemical production where poisonous or otherwise dangerous substances are handled. The development of solid electrodes, which permit polarographic analyses of high melting materials or of substances which react with mercury, is emphasized in this paper and in other recent Russian work on the subject.

A mercury electrode can be used only up to potentials at which oxidation of the mercury itself begins. At higher potentials an electrode of some other materials, for instance platinum, must be used. A disadvantage of the solid electrode is the easy contamination of the surface. In order to establish stationary diffusion, it is advisable to rotate the electrode at some definite velocity.

The limiting current density at a rotating disk electrode can be expressed by the following equation (1):

$$I_{lim} = D_1 n F c \frac{1}{1.61 D^{2/3} \nu^{1/6} \omega^{-1/2}}$$

Here D_1 is the diffusion coefficient of the reacting substance, D the diffusion coefficient of the electrolyte, ν the kinematic viscosity of the liquid, and ω the angular velocity of electrode rotation. The accuracy of this equation and its applicability for determining either the concentration or the diffusion coefficient of the reacting ion has been demonstrated in the case of a rotating amalgamated copper electrode (2).

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The limiting diffusion current is directly proportional to the concentration of the substance participating in the electrode reaction (c) and to the number of electrons participating in the reaction (n):

$$I_{lim} = Knc$$

The use of solid electrodes opens new possibilities as far as the study of organic substances is concerned. For instance, by using as an anode a rotating platinum needle five millimeters long and having a diameter of 0.5 millimeters, and as a cathode a cadmium plate having an area of four square centimeters, the anodic oxidation of hydroquinone, which results in clearly defined polarographic waves, could be demonstrated (3). Distinct oxidation waves could also be obtained with ascorbic acid and pyrocatechol.

The polarographic method has recently been introduced into the study of kinetics of chemical reactions. Thus, during the induction period of a cold butene-2 flame, organic peroxides and aldehydes collect in the mixture. These could be determined by reduction at a dropping mercury cathode (4). Peculiarities in the behavior of unsaturated aldehydes under polarographic examination permitted the detection of croton aldehyde in the oxidation products of butene-2, thus showing that an atom of oxygen may combine with the terminal carbon of butene-2 rather than react at the double bond (5). In a similar manner the oxidation of propylene (6) and of propane (7) was investigated.

By photographing graphite or coal particles suspended in the liquid, the velocity and type of motion of the liquid near the drop electrode were determined (8, 9, 10). By using this method, the fact that two types of maxima arise was demonstrated. Maxima of the first kind are produced because the polarization in the upper part of the mercury drop is different from that in the lower part, bringing about motion of the mercury surface due to the resulting surface tension gradient. The so-called maxima of the second kind arise in sufficiently concentrated solutions due to tangential movement of the mercury surface. This effect depends on the rate of mercury flow, i.e., the pressure under which the mercury flows out.

In view of the fact that surface active compounds suppress maxima of the second kind, it is possible to determine the adsorption of surface active compounds on a dropping mercury electrode by using this property. The presence or absence of a current producing a maximum of the second kind can be used for determining the purity of water (11). This method permits the determination of surface active compounds present in a concentration of 10^{-9} mols per liter. Surface active compounds are adsorbed only in a definite potential range within which inhibition of movement of the mercury surface and suppression of maxima are possible (12). The limits of this range coincide with an abrupt change in the capacity of the double layer and an increase of the limiting current. Interesting cases of the effect of adsorption of surface active compounds on kinetics of the separation of metals at the mercury surface have been investigated (12).

A number of recently published papers dealt with the investigation of kinetics of electrode processes by means of an alternating current. An alternating current is preferable to a direct current, because with the latter, measurement of a reaction rate becomes impossible when the velocity of an electrode reaction exceeds that of the diffusion current supplying the reacting substances. By selecting a current frequency which is high enough, it is possible to lower the concentration polarization sufficiently to permit measurement of the reaction rate itself. Work in this field by B. V. Ershler (13, 14), who has developed the theory of polarization of reversible electrodes by weak alternating currents, is outstanding.

Before a polarographic determination is carried out, it is necessary to remove oxygen from the solution by blowing through hydrogen or nitrogen. This

results in losses of volatile substances. If the volatile substance is to be determined polarographically, a special construction of the cell becomes necessary. Several such constructions were proposed recently (15, 16).

Frequently waves of an insufficient height are produced in a polarographic analysis, so that the determination of some substances becomes difficult. In order to increase the height of the waves, an electrode vessel equipped with a number of capillaries may be used (17). A multistream mercury electrode can be constructed by using a porous glass filter. An electrode of this type was applied in studying the kinetics of the reduction of halogenated organic substances (18).

The values of the mass of mercury flowing out per second (m) and of the time of drop formation (t) vary with the electrode potential, the height of the capillary, and other factors. In order to regulate m and t and to keep them constant, a spatula-like appliance can be attached to the capillary. With this arrangement, the drops grow only to a certain uniform size before falling (18). The same end can be achieved by using a wide capillary which is provided with a constriction near the tip, so that the rate at which mercury drops flow out is greatly reduced. The drops are detached by a rod tapping the upper end of the capillary (19). When m and t were regulated by either of the two methods described above, the maxima on the curves $I = f(E)$ disappeared.

The interest in solid electrodes for polarographic work has already been mentioned. E. M. Skobets and his collaborators (20) have worked on various types of stationary and moving solid microelectrodes. The best results as far as elimination of sharp maxima is concerned were obtained with an amalgamated silver drop-shaped cathode or an amalgamated platinum needle under conditions of rectilinear motion of these electrodes with reference to the solution.

Organic polarography has developed to such an extent that it promises to be of considerable aid to analysis and production control in the synthetic organic industry.

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